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Low-Emission Floor Covering

Description

The present invention relates to a floor covering, which has excellent wear resistance and essentially causes no malodorous and/or health impairing emissions and is not subject to color changes due to aging over a longer period of time, as well as a process for manufacturing the same.

Rubber-based elastomer floor coverings are among the high-performance floor coverings due to their durability and wide range of applications. However, vulcanization and process additives or agents tend be released from the floor covering in unchanged or chemically changed form.

Typically, vulcanizable rubbers of a wide variety of types are used as polymeric binders for floor coverings. These rubbers include primarily SBR, NR, IR, IIR and NBR, the cross-linkage of which is achieved by cross-linking agents, such as sulfur, in conjunction with vulcanization additives. Such vulcanization additives include vulcanization accelerators, e.g., mercapto compounds, sulfenamides, thiuram, guanidine, dithiocarbamates and amines, vulcanization retarders, e.g., phthalic acid anhydride and N-cyclohexylthiophthalimide, antioxidants, e.g., 2-mercaptobenzimidazole, masticating agents, e.g., 2,2'-dibenzamidodiphenyl-disulfide, softeners or process oils, reinforcing resins, e.g., phenol formaldehyde resin, and in part vulcanization activators, e.g., zinc oxide. These vulcanizing agents and additives are not completely converted in the vulcanization process. As a result, these additives or their byproducts produced in the vulcanization process partly remain in the system or are released from this rubber system. This emission process may continue over a relatively long time. In floor coverings, this occurs especially when they are taken out of their packaging and by means of

adhesives are fixed to the floor on a suitable substrate. Temperature, air humidity and ventilation of the room further influence the progress of the emission process.

Generally, the vulcanization additives or their byproducts produced during the vulcanization process, which are released from the rubber system, cause an unpleasant odor and are a health hazard at certain concentrations. It has also been shown that substances released from rubber floor coverings may cause white walls (plaster, wall paint, etc.) to yellow. Furthermore, these rubber-based elastomer floor coverings are subject to aging, which negatively affects the color of a patterned floor covering, e.g., by yellowing.

Thus, the object of the present invention is to provide a wear-resistant, low-emission, non-aging and variably color-patterned floor covering with an attractive appearance having elastomeric, rubber-like properties without the presence of rubber vulcanized with sulfur or sulfur compounds.

This object is attained by the embodiments characterized in the claims. In particular, a floor covering is provided comprising at least one elastomer as polymeric binder based on at least one polyolefin with a density < 0.910 g/cm^3 and at least one graft copolymer. Preferably, a polyolefin with a density ranging from 0.85 – 0.91 g/cm^3, particularly preferably from 0.85 – 0.892 g/cm^3 is used. The polyolefin is preferably selected from among the class of the VLD PE polymers.

According to a preferred embodiment, the polyolefin is a mixture of at least two ethylene copolymers, wherein the ethylene copolymer comprises a copolymer (a) as the main polymer with a density of 0.89 – 0.91 g/cm^{3}and, a copolymer (b) to control rheology and elasticity with a density of 0.86 – 0.88 g/cm^3 and a MFI > 3 (at 190°C; 2.16 kg).

For example, the copolymers (a) and (b) are copolymers of ethylene and octene. The copolymers (a) and (b) can be present, for example at a weight ratio of 4:1 to 3:2.

To increase wear resistance, the polymeric binder contains as a further component at least one graft copolymer, preferably based on a HD polyethylene. In particular, the graft copolymer can be a HD polyethylene grafted with maleic acid anhydride, where the grafting degree is preferably 1% to 5%. The proportion of graft copolymer is, for example, 5% to 25% by weight in relation to the total weight of the polymeric binder. Accordingly, the proportion of the at least one polyolefin, which in addition to the graft copolymer constitutes the polymeric binder of the floor covering according to the invention, is between 75% to 95% by weight in relation to the total weight of polymeric binder.

The polymers used to construct the floor covering according to the invention, i.e., the at least one polyolefin in combination with the at least one graft copolymer is cross-linked with at least one suitable cross-linking agent based on organic peroxides, particularly organic peroxides free from aromatic hydrocarbons, and possibly one or several co-cross-linking agents. An example of a suitable organic peroxide, free from aromatic hydrocarbons, is the commercially available DHBP (2,5-dimethyl-2,5-di(tert.butylperoxy)hexane). Isocyanuric acid derivatives and/or acrylate or methacrylate derivatives, derived from polyols, may be used as co-cross-linking agents. Particularly preferred as a cross-linking agent, this is a mixture of one part by weight of organic peroxide free from aromatic hydrocarbons, two parts by weight of trimethylolpropane trimethacrylate (TRIM) and one part per weight of triallyl isocyanurate (TAIC). TRIM influences the hardness and the indentation characteristics of the elastomer constituting the floor covering according to the invention, whereas TAIC has a positive effect on the cross-linking rate.

Polyolefins suitable for use in the floor covering according to the invention are, for example, the following commercially available polymers: DOW DSH 1500, DOW DSH 8501, Exxon Exact 4041 and Exxon Exact 4033. Preferred components for the aforementioned ethylene copolymer are, for example, DOW DSH 1505 as copolymer (a) and DOW EG 8200 as additional copolymer (b), which may be used to control rheology and elasticity. A suitable graft copolymer for use in the floor covering according to the invention is, for example, the commercially available polymer DOW XU 60769.07.

The floor covering according to the invention can furthermore contain fillers or a mixture thereof, particularly a mixture of platelet-shaped and crystalline mineral intergrowths, which as reinforcing fillers substantially contribute to the properties, particularly to the mechanical properties, of the floor covering according to the invention. The filler amount used is 35% to 60% by weight in relation to the total weight of the composition or formulation forming the floor covering according to the invention, where a minimum proportion of platelet-shaped filler particles is necessary to reach higher filler amounts. Examples of such fillers are:

- Sillitin, available from Hofmann Mineral,
- Doltitan 2, available from PETROCHEM K. Zafranas S.A.,
- Inducarb 2, available from Omya, or
- Kronos 2200, available from Kronos Titan.

Other fillers, which the floor covering according to the invention may contain, are for example:

Filler	Type (e.g.,)	Supplier
Quartz powder	Sirkon SF 300	Quarzwerke GmbH
Kaolin	Nucap EDL 200	Lehmann & Voss & Co.
Talcum	Alpha Talc CT 6/46	Alpha-Calcit Füllstoffe GmbH KG

Wood flour	Holzmühle Westerkamp & Co.	Wood flour Type 120
Dolomite	KL 30	Naintsch Mineralwerke Graz
Aluminum trihydroxide	Martinal ON 313	Martinswerk GmbH
Precipitated silicic acid	P 820	Degussa AG
Heavy spar	Heavy spar TS	Sachtleben GmbH
Chalk	Omyacarb 6	Omya

Furthermore, depending on the color adjustment, the floor covering according to the invention may contain the following inorganic pigments:

Pigments	Supplier
Kronos 2200	Kronos Titan
Bayferrox 140	Bayer AG
Bayferrox 830	Bayer AG
Hostaprint A2 R 31	Clariant

Where indicated, the floor covering according to the invention may also contain conventional processing agents. The following are examples of such processing agents:

Slip Additives	Type (e.g.,)	Supplier
Ca stearate	Ceasit 1	Bärlocher GmbH
Ester wax	OP wax	Clariant

In addition, antioxidants, UV stabilizers and the like may be contained:

Stabilizers	Type (e.g.,)	Supplier
Antioxidants	Irganox 1010	Ciba Geigy AG
UV stabilizers	Chimassorb 944 FI	Ciba Geigy AG

Based on the elastomer used as polymeric binder according to the invention, the inventive floor covering exhibits practically no malodorous and/or health impairing emissions, in contrast to the known floor coverings that use rubbers (SBR) as elastomers. In addition, the floor covering according to the invention has excellent abrasion resistance compared to the known rubber-based floor coverings. Due to the subsequent cross-linkage of the polymers constituting the, at least, one elastomer and used as polymeric binder in the floor covering according to the invention, it is possible, surprisingly, to increase the filler amount in the floor covering up to 60% by weight in relation to the total weight of the composition or formulation forming the floor covering according to the invention while maintaining excellent wear behavior.

Surprisingly, the surface energy of the floor covering thus produced can be very readily increased by a corona treatment, so that a primer exhibits very good adhesion resulting in better bondability compared to rubber floor coverings. Surprisingly, it was also found that the floor covering according to the invention is less subject to color changes (yellowing) during its life. Thus, it is possible to achieve sufficiently flexible pattern and color design possibilities, adequate resistance to aging and low emission loads while nevertheless retaining the desired elastomeric properties.

A further subject of the present invention is a process for producing the floor covering according to the invention comprising the provision of substrates in the form of strips and the application of the above-defined elastomer to one side of the substrate.

For the substrate, any material currently used in floor coverings and based on natural and/or synthetic woven or knit fabrics, textile materials as well as fleece or nonwovens may be used. For example, jute fabrics or blends of natural fibers, such as cotton and staple fibers, glass fiber fabrics, glass fiber fabrics coated with adhesion promoters, synthetic blends, fabrics made of core/sheath fibers, e.g., with a polyester core and a polyamide sheath.

Furthermore, a novel process for manufacturing a low-emission, particularly homogenous floor covering is provided, comprising essentially the following steps:

- Wetting of particles with a solution containing at least one organic peroxide free from aromatic hydrocarbons and possibly one or more co-cross-linking agents and possibly process oil, where the particles contain the above-defined polymers forming the polymeric binder of the floor covering according to the invention, either uncross-linked or partially cross-linked, in the form of a ground or granulate stock,

- Heating of the particles to a temperature at which the peroxide has sufficiently long stability, and subsequent compaction of the particles and shaping into a flat product, and

- Pressing of the flat product thus obtained in a suitable apparatus at a temperature at which the half-life of the peroxide is reduced, such that cross-linking initiated by the peroxide simultaneously occurs, to obtain a flat final product.

In particular, the process according to the invention, in a preferred embodiment, can comprise the following steps (a) to (d). In step (a) a cross-linkable mass containing the above-defined polymeric material, fillers and at least one peroxide

for pre-cross-linkage and possibly process-promoting additives are compounded in a suitable apparatus such as, for example, an extruder, to produce a ground or granulate stock. For extruder compounding, a unidirectionally rotating ZE 40x39.5 D twin-screw extruder may be used, for example. The feed zone is heated to approximately 140° – 175°C, the further zones up to the nozzle to 195°C. The screw speed typically ranges from 60 to 80 rpm. The exiting slab is cooled in a water bath and granulated in the slab granulator. The granulate thus obtained, can be further ground to achieve certain structures prior to wetting with peroxide.

Subsequently, in step (b), the ground or granulate stock thus obtained (hereinafter also referred to as "particles") is wetted with a solution containing at least one organic peroxide that is free from aromatic hydrocarbons and, optionally, co-cross-linking agents and possibly process oil. This permits the migration of the peroxide and the co-cross-linking agent into the particles of the ground or granulate stock. The granulate mixture, the particles of which may differ in their degree of pre-cross-linking, is heated in a granulate drier to a temperature of about 50°C. The hot granulate is then introduced into a slow-running horizontal mixer and wetted with a liquid mixture of co-cross-linking agents and possibly process oil and mixed for about 30 minutes. This is followed by wetting with peroxide and possibly process oil and further mixing for about 10 minutes. After a total mixing time of about 40 minutes, the liquid mixture has diffused into the granulate particles. Prior to further processing, the granulate is then intermediately stored for at least 48 h, preferably in a heat insulated container for slower cooling.

In step (c) the particles are heated to about 50°C and then precompacted and shaped, for example in the nip of a two-roll mill. The rolls typically have a surface temperature of 130° – 170°C. The roll surface can be smooth or corrugated/crisscrossed. For the corrugated roll, the lower surface temperature

applies. The structure of the flat shape produced in the roll nip is a function of the diameter and the surface characteristics of the rolls. With smooth rolls, the structure is a function of the degree of pre-cross-linking. The mass in the bead, however, should not be hotter than the scorch temperature of the peroxide used in step (b). In this step, a coherent sheet without holes and with close weight tolerances per unit area across its width is usually produced. The surface of the rolled sheet, however, does not usually need to be smooth. A rough surface actually enhances breathing in the following process step.

In the next step (d) the material thus heated is smoothed and cross-linked in an apparatus, such as a twin press, multi-platen press, twin Auma or steel band Auma machine, at a suitable pressing power of, for example, 1.2 – 5 bar/cm^2 and at a temperature of, for example, 180° – 200°C, at which the half-life of the peroxide is reduced, such that simultaneous cross-linkage of the material initiated by the peroxide occurs. Due to the high heat capacity of the filled polymeric binder masses, the corresponding strips are usually preheated to a temperature of about 160°C prior to introducing them into the aforementioned apparatuses. The speed of the above Auma machines or presses is a function of the half-life of the employed peroxide at the correspondingly selected temperature within the strip cross-section as it passes through the machine.

In another embodiment, the addition of co-cross-linking agent(s) can occur already in step (a) without any further addition of co-cross-linking agent being required in step (b) as described above, which makes it possible to shorten the mixing time.

In a further embodiment, an excess of co-cross-linking agent, particularly trimethylolpropane trimethacrylate (TRIM) may be used. The molar ratio of peroxide to co-cross-linking agent is at least 1:4. The non-reacting TRIM excess acts as a processing aid and reduces the viscosity of the polymer melt prior to

the addition of peroxide in the extruder. In the subsequent processing step in the course of the production of the floor covering according to the invention, i.e. the wetting of the additionally ground extruder granulate with liquid peroxide and the subsequent cross-linking of the flat product, the TRIM contained in the particles reacts with the diffused peroxide. It is therefore unnecessary to rewet the ground stock with co-cross-linking agents. During pre-cross-linking in the compounding extruder, the following raw material addition sequence has proven to be suitable. Through the first metering orifice of the extruder, a master batch of additives, such as slip agents, antioxidants and static eliminators are added in addition to the polymer mixture. Here, too, a co-cross-linking master batch may be added, such as, for example, Perkalink 301-50 (a 50% preparation of triallyl isocyanurate). After the melting section in the extruder, the liquid co-cross-linking agent, such as, for example, TRIM, and possibly mineral oil, are added via an injection nozzle. To this polymer melt the viscosity of which is reduced due to the added liquids, the filler is added, for example via a lateral feed unit. Prior to feeding the filler into the polymer melt, it is preferably mixed with the pre-cross-linking peroxide in the form of a powdered master batch. This ensures uniform distribution of the reactive components. Between the lateral feed unit and the vacuum degasification unit on the extruder, a sufficiently long section for mixing and reaction can be disposed to promote uniform distribution through a specially adapted temperature profile and a specific design of the screw profile.

In another embodiment of the process according to the invention, instead of the shaping in the roll nip executed in step (c), the wetted particles can be distributed onto a leader and covered with an embossed anti-adhesive paper to produce a non-directional design of the floor covering. The granulate feed stock is compacted in the press while cross-linking and is pressed for a corresponding dwell time. Subsequently, the bottom leader and the top release paper can be pulled off.

In one embodiment of the process according to the invention, partially cross-linked particles based on the above-defined polymeric material comprising polyolefin and graft co-polymer are added to the uncross-linked mass to obtain a relief structure of the flat product after pressing in step (d). The partially cross-linked particles can be cross-linked to a varying degree. Partial cross-linking of the particles can occur during extruder compounding prior to granulation in the case of granulate. The partially cross-linked particles are only reversibly deformed during pressing, and after pressure release, due to the restoring forces, a high/low structure is obtained. The degree of cross-linkage of the partially cross-linked particles may be adjusted via the peroxide amount and the possibly used co-cross-linking agents.

In a further embodiment of the process according to the invention, in step (a), a cross-linkable mass based on the above-defined polymer materials is compounded with at least one cross-linking agent and possibly one of the above-defined additives. By controlling the dwell time in the extruder, and through a corresponding screw geometry, and overall length of the extruder it is possible to obtain a partially cross-linked granulate. This embodiment permits the production of patterns analogous to PVC technology. This means, for example, that a directional structure can be obtained. In this embodiment it is possible, in particular, to combine the mechanical properties of elastomer coverings with the visual/structural characteristics of PVC coverings.

By using an uncross-linked or partially cross-linked mass, i.e. a cross-linkable mass without peroxide or with a very small amount of peroxide, it is possible to control the course of the process via the migration of the peroxide used in the solution to sheathe the particles of ground or granulate stock. Furthermore, the multi-stage production process allows the use of equipment or apparatuses that are typically used in the soft PVC industry.

In another embodiment of the process according to the invention, the mass can be compounded in step (a) with an added chemical expanding agent, such as, for example, sulfohydrazides or azodicarbonamides or a combination therefore, e.g., Luvopor 1417 (Lehmann & Voss & Co.) or Tracel DB 145 (Tramaco GmbH). After cross-linking under pressure in step (d), foaming of the material is achieved by pressure release at a further increased temperature. This embodiment is particularly suitable for floor coverings with expanded backing.

To produce a foam granulate for coverings with integral structure, a mixture of the aforementioned polymers, additives, e.g., slip agents, antioxidants and static eliminators, fillers, peroxide, co-cross-linking agents, e.g., methacrylate or TAIC, and a chemical expanding agent, e.g., azodicarbonamide, are compounded in an extruder. By a corresponding extruder design and adapted operating conditions, the mixture is partially cross-linked in the extruder and expanded and then delivered through the extruder nozzle in the form of a foam. As with compact material, the slap is cooled in a water bath and granulated. The granulate thus obtained is further ground and dried and subsequently wetted with a mixture of liquid peroxide, co-cross-linking agents and mineral oil. The ground stock is distributed onto release paper, covered with a release paper and fed into a heated press or the like. The temperature and pressure are adjusted such that the particle bed becomes plastic along the heating surfaces and melts to form a closed surface. At the same time, the temperature initiates the decomposition of the peroxide whereby the outer layers simultaneously cross-link. The low pressing power and the onset of the cross-linking reaction prevent a compression of the foamed material in the core of the plate thus obtained. This is further supported by a correspondingly high pre-cross-linking of the foamed material. This makes it possible to provide an elastomer covering with an abrasion-resistant wear layer and, at the same time, reduced density and improved impact sound characteristics.

In the aforementioned apparatus, embossing may be carried out at the same time, preferably by using a corresponding release paper. The thermoplasticity of the mass that still exists prior to the actual cross-linkage is sufficient to smooth the rolled sheet or to form the embossing before the onset of the cross-linking reaction.

In a finishing step, depending on the quality of the rolled sheet obtained in step (c), the back of the covering may have to be ground for sizing. Furthermore, the structure or pattern of the cross-linked material may be revealed after exposing the surface by grinding and or splitting. To improve bondability, a corona treatment with primer application may be carried out.

Special, heterogeneous floor covering structures may also be provided based on the present invention. The lay characteristics can be positively influenced by a correspondingly adjusted degree of cross-linking of the individual layers. To secure this effect, a suitable measurement procedure was developed in the context of this invention. Samples of the corresponding structure and thickness measuring 250 mm x 250 mm are produced. Parallel to the sample edges, sensors for an incremental length-measuring system are pasted to the surface at a 90° angle. The sample is conditioned in a standard 23/50 environment on a glass plate powdered with talcum. Subsequently, the samples are exposed to changing temperatures (10° to 60°C) and humidity conditions (35% to 90% relative humidity) in a climactic chamber and the expansion behavior is recorded. This measuring method makes it possible to predict the lay behavior of a floor covering thus produced already in the development stage and to optimize the covering formula and the correspondingly adjusted process.

The following multi-layer structures were developed and tested by means of the aforementioned measurement procedure: a mixture of multicolored particles of different sizes was distributed over a homogenous, calandered substrate and

compacted. If desired, a transparent layer may be applied over it in the form of a distributed powder or by foil lamination. Alternatively, a conventional multilayer structure of different foils that are joined by applying pressure and heat may also be used. The multilayer structures, the cross-linking degree of which can be optimized by the described measurement procedure, further permit the production of dimensionally stable tiles based on the polymers used to make the floor covering according to the invention.

Even when producing the floor covering according to the invention in the form of a homogeneous covering by distributing granulate or ground stock over a strip with release properties, structure variants can be produced through the distribution of the corresponding particle fractions, i.e. by distributing first the basic color(s) and subsequently the particles in contrasting colors. This can be achieved in that the basic color is distributed over a substrate via a distributing unit with a brush roller uniformly arranged across the width. This applies the basic color in a weight distribution that is uniform over the width of the strip. The contrasting particles are then also distributed, but the distributing unit is preferably designed in such a way that different particle amounts are applied across the width of the strip. Subsequently, the particle bed is precompacted and fed into a heated press or the like. Alternatively, the two distributing units for the particle bed can be formed in such a way that a lesser amount of the basic color(s) is applied in the areas in which the contrasting particles are going to be distributed. When the contrasting particles are subsequently distributed, a particle bed that is uniform across the width is achieved. With this second variant, in particular, it is possible to achieve a non-warping structure and uniform thickness across the width of the strip even without precompaction. Other interesting structures can furthermore be achieved during installation by stamping two or four tiles of equal size across the width of the material.

The present invention will now be explained in greater detail by means of the following example.

Example

A homogeneous mixture is produced and granulated from the following ingredients:

DOW DSH 1505	1875.0 g
DOW EG 8200	750.0 g
DOW XU 60769.07	375.0 g
Sillitin Z 89	1500.0 g
Omyacarb 6 BG	1125.0 g
Kronos 2200	375.0 g
Glycerol monostearate	48.0 g
Hostastat FA 14, 50%	12.0 g
Wax OP	36.0 g
Perkadox 14-40 BPD	10.2 g

The above formula was compounded in a type ZE 40 of the Berstoff company unidirectionally rotating twin-screw extruder with simultaneous pre-cross-linkage through the added peroxide. The cylinder temperature of the extruder in the feed zone was 145°C and in zones 3 – 9 195°C. The speed was 80 rpm.

The granulate thus obtained, after drying and preheating to 50°C, was wetted with a mixture of TAIC (triallyl isocyanurate) and TRIM (trimethylolpropane trimethacrylate) and mixed for about 20 minutes. Subsequently, a mixture of

Trigonox 101 and Dealen CP 31 N was added and mixed for another 10 minutes. The quantity ratios in relation to 500 g granulate were as follows:

TAIC	1.0 g
TRIM	3.0 g
Trigonox 101	4.0 g
Dealen CP 31 N	1.0 g

After a 48 h interim storage period, the wetted granulate was pressed into a plate in a static press at 140°C, and this plate was then also cross-linked in a press at 185°C for 10 minutes. Of this 140°C plate, a sample was measured on the Göttfert "Elastograph Vario" at 185°C. The adjusted measuring time was 12 minutes; the deformation angle was 0.4°. The T90 time for this mixture was 2.9 min., Tv_{max} at 0.7 min.

In the test specimen of the elastograph, the indentation characteristic was measured in accordance with EN 433. The initial thickness was 6.35 mm, the indentation after 150 minutes was 0.27 mm, and the remaining indentation after release for 150 minutes was 0.01 mm. This results in an index of 4.3 and a recovery of 95.1%.

From the cross-linked plate, S2 rods were stamped. The Shore A hardness was 95, the Shore D hardness 46. The 2.23 mm thick S2 rod exhibited a load at break of 12.7 N/mm^2 and an elongation of 430%.